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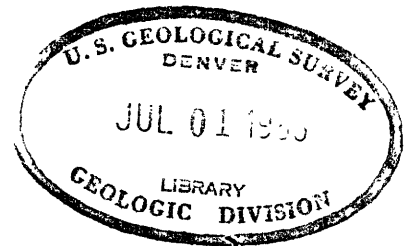
UNITED STATES DEPARTMENT OF THE INTERIOR
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SOME QUANTITATIVE ASPECTS OF THE OXIDATION AND
REDUCTION OF COLORADO PLATEAU ORES*

By

R. M. Garrels and A. M. Pommer

May 1956



Trace Elements Investigations Report 177

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SOME QUANTITATIVE ASPECTS OF THE OXIDATION AND
REDUCTION OF COLORADO PLATEAU ORES

By R. M. Garrels and A. M. Pommer

ABSTRACT

Equations illustrating the oxidation of many minerals of the ores are presented, and the "oxygen demand" for complete oxidation of a representative uraninite-montroseite-pyrite-vanadium clay ore is calculated. Approximately 100 to 150 pounds of oxygen are required per ton of ore. From considerations of the rate at which oxygen can be supplied by ground water as opposed to that from air circulation in unsaturated rocks, it is concluded that significant oxidation below the water table is not likely.

Experiments on the reduction of quinquevalent vanadium solutions by fresh Norway spruce and a North Dakota lignite at 120 to 150° C show that both materials are effective reducing agents. Their experimentally determined reducing capacity in runs lasting a few days is approximately half the theoretical reducing capacity calculated on the assumption of complete oxidation to CO_2 and H_2O . The conclusion is reached that about 0.5 weight percent of lignite is sufficient to form a typical uranium-vanadium ore by reduction of uranium (VI) and vanadium (V) or (IV) in solution to uraninite and montroseite, respectively. Subbituminous or higher rank coal may be expected to behave in a similar fashion.

INTRODUCTION

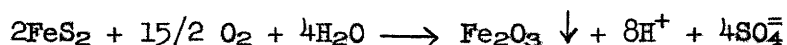
The mineralogic and chemical changes during oxidation of the Colorado Plateau uranium deposits are now known in considerable detail. The primary ore minerals are chiefly low-valence uranium, vanadium, iron and copper compounds. In the first part of this paper the probable chemical reactions that occur during oxidation are assembled, and estimates are made of the quantitative oxygen requirements for maximum alteration of a typical ore. The latter part is devoted to study of a process that may have been important in ore deposition, namely, the reducing effect of woody materials.

OXIDATION OF URANIUM ORES

Oxidation of uranium ores involves chiefly the oxidation of pitchblende (UO_2), montroseite (VOOH), vanadiferous chlorite, vanadiferous hydromica, pyrite (FeS_2), and chalcopyrite (CuFeS_2). Many other minerals are present in small amounts from mine to mine, but oxidation of the six chosen probably constitutes more than 90 percent of the oxygen demand. They serve also as examples for the other compounds. The oxidation equations, plus some of the subsequent reactions with wall-rock constituents, are given in sequence for the individual minerals. A few notes on the environment of oxidation are included.

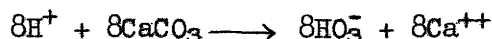
Pyrite

Pyrite usually oxidizes to produce ferric oxide or hydrated ferric oxide. Jarosite is important locally. From the reaction:

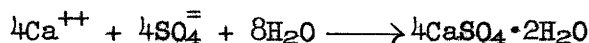


it is evident that every mol of pyrite produces 4 mols of hydrogen ion.

If calcite is present, as is common, it is dissolved to give bicarbonate ion and calcium ion in solution:

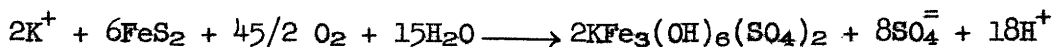


Some of the Ca^{++} commonly reacts with SO_4^{--} to give gypsum:



Reaction with calcite tends, then, to give gypsum and a neutral or slightly alkaline solution with residual dissolved Ca^{++} . If calcite is absent or sparse, the hydrogen ions may attack clay or feldspar. Little is known of the process in Plateau deposits, although it may be an important reaction.

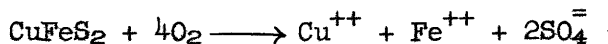
The reaction to form jarosite requires K^+ from the environment:



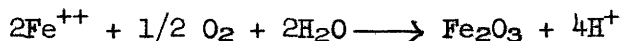
Free acid is formed, as in the oxidation of pyrite to Fe_2O_3 , but each mol of pyrite produces 3 mols of hydrogen ion. It is probably necessary to use up most of the acid produced by reaction with minerals such as calcite, if jarosite is formed as a stable solid.

Chalcopyrite

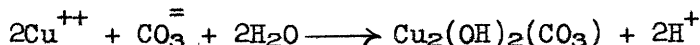
In the oxidation of chalcopyrite, iron and copper are released when sulfide goes to sulfate. Iron is usually precipitated as ferric oxide or hydrated ferric oxide, whereas copper reacts with carbonate and hydroxyl ions to form malachite or azurite. For chalcopyrite:



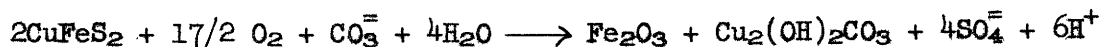
The Fe^{++} oxidizes to Fe^{+++} and hydrolyzes to ferric oxide:



Cupric ion reacts with water and carbonate ion in solution to form malachite:



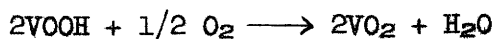
The over-all reaction is:



Montroseite

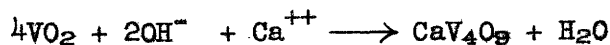
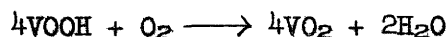
Montroseite oxidizes in a complex manner. Evans (1956, fig. 12), shows the minerals formed and some of the possible pathways. Here many of the individual reactions are given. They then can be used for calculation of oxygen demand for a given stage of oxidation along a desired pathway.

Montroseite to paramontroseite.---As shown by Evans and Mrose (1955, p. 872), montroseite alters pseudomorphously to paramontroseite by loss of hydrogen from the structure:

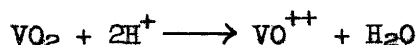


Montroseite to simplotite.---Under slightly alkaline conditions montroseite may oxidize to the calcium vanadite simplotite, for at a pH of about 8 vanadium (IV) behaves as an anion. Direct oxidation is not likely; paramontroseite probably precedes formation of other vanadium (IV) species.

Paramontroseite may dissolve under slightly alkaline conditions and reconstitute to simplotite by combining with Ca^{++} :



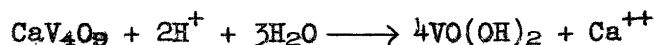
Montroseite to duttonite.---Duttonite, a vanadium (IV) hydroxide, has been recognized. It may form by solution of paramontroseite under either alkaline or acid conditions, with reprecipitation by neutralization. Paramontroseite may dissolve under the influence of acid from pyrite:



Then reprecipitation by increase in pH would give:

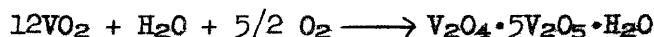


Alternatively, simplotite might be converted to duttonite by decrease in pH:

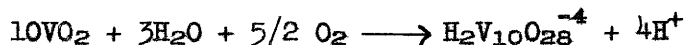


Paramontroseite to mixed vanadium (IV) and (V) oxides.---It appears

that paramontroseite is the most common first oxidation product of montroseite and that further oxidation reactions probably involve paramontroseite more frequently than duttonite or simplotite. Under neutral or acid conditions part of the vanadium (IV) apparently oxidizes to vanadium (V) containing anions, which react with the vanadyl ion $(\text{VO})^{++}$ to form vanadyl vanadates. The formation of many compounds is possible, and many actually do form as indicated by the complex corvusite group of mixed vanadium (IV) and (V) oxides. The summary equation of a typical reaction might be:



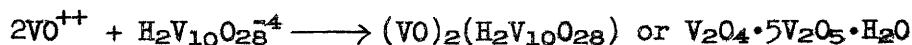
According to the postulated mechanism the reaction takes place in two steps. First, some of the paramontroseite is oxidized to a vanadate ion:



The reaction of some of the remaining paramontroseite with water produces some vanadyl ions:



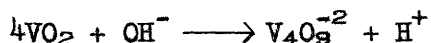
Then the vanadyl ion combines with the vanadate ion to form vanadyl vanadate (a member of the corvusite group):



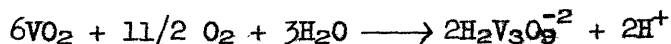
The great variety of species possible becomes evident when it is considered that VO^{++} ion might react with $\text{H}_2\text{V}_{10}\text{O}_{28}^{-4}$ as indicated, or with

$\text{H}_3\text{V}_{10}\text{O}_{28}^{-2}$, as well as with such vanadate ions as $\text{V}_4\text{O}_{12}^{-4}$, $\text{HV}_4\text{O}_{12}^{-3}$, or $\text{H}_2\text{V}_4\text{O}_{12}^{-2}$, to mention but a few (Evans, 1956). However, most combinations in the neutral or acid range would be expected to produce compounds with a $\text{V}_2\text{O}_5/\text{V}_2\text{O}_4$ ratio of 3 or higher, the ratio increasing with decreasing pH.

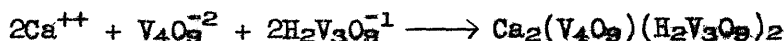
Paramontroseite to metal vanadite-vanadates.---The reactions to form mixed vanadium (IV) and (V) compounds so far discussed involve reaction between V^{+4} as a cation (VO^{++}) and vanadate ions. Inasmuch as vanadium (IV) also occurs as anions in such minerals as simplotite (CaV_4O_9), there is a possibility of forming compounds by reaction among metal ions, vanadite ions ($\text{V}_4\text{O}_9^{-2}$ or $\text{HV}_4\text{O}_9^{-1}$), and vanadate ions. Again the probable complexity is apparent. However, a typical reaction might be described in steps. First, paramontroseite could react with hydroxyl ions to form vanadite ions:



Also, paramontroseite could be oxidized to a vanadate ion:



The metal ions, such as calcium, could combine with the vanadite and vanadate ions to form a mineral such as melanovanadite:



This also can be written as $2\text{CaO} \cdot 2\text{V}_2\text{O}_4 \cdot 3\text{V}_2\text{O}_5 \cdot 2\text{H}_2\text{O}$.

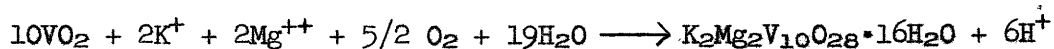
In general, such metal vanadite-vanadates have a lower ratio of $\text{V}_2\text{O}_5/\text{V}_2\text{O}_4$ than the vanadyl vanadates and probably form at higher pH.

Paramontroseite to metal vanadates.---With sufficient oxygen available, the complex of mixed vanadium (IV) and (V) compounds is oxidized completely to metal vanadates, such as hewettite, hummerite, pascoite, and rossite. Over-all reactions are presented for the oxidation of paramontroseite to some of the chief metal vanadates.

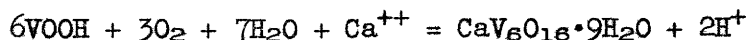
For paramontroseite to hewettite:



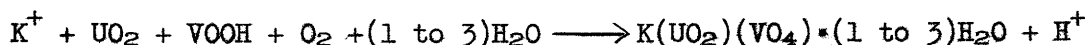
For paramontroseite to hummerite:



Montroseite to metal vanadates.---The over-all reaction from montroseite to metal vanadates shows the total oxygen demand. The change to hewettite is typical:

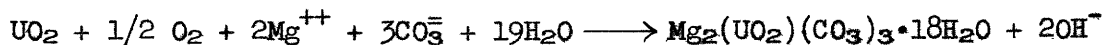


Pitchblende and montroseite to carnotite.---The over-all reaction from original pitchblende and montroseite to carnotite is:



One mol of pitchblende and one mol of montroseite thus require one mol of oxygen to form one mol of carnotite.

Pitchblende to uranyl carbonate, sulfate, or silicate.---In the presence of excess vanadium, oxidation of pitchblende yields only carnotite or tyuyamunite. If vanadium is absent, uranyl carbonates, silicates, or sulfates may form. For all such uranyl compounds, the oxygen demand is 1/2 mol O_2 for each mol of pitchblende. A typical reaction is the oxidation of pitchblende to form bayleyite:



Vanadium mica, vanadium hydromica,
and vanadium chlorite

Details of oxidation of the vanadium silicates are not known, but some inferences can be drawn from the chemical analyses (Foster, 1956). Vanadium mica (roscoelite) contains vanadium (III) and apparently is not altered at a finite rate by ordinary oxidation processes. Vanadium

chlorite and vanadium hydrous mica are found by analysis to contain vanadium (IV) and a mixture of iron (III) and iron (II). According to Foster's interpretation, the vanadium entered the structure as V(IV), in which case only enough oxygen would be used to change iron from Fe(II) to Fe(III). If, on the other hand, the iron and vanadium originally were Fe(II) and V(III), the maximum oxygen demand would be that necessary to change the vanadium to V^{+4} and the iron to Fe^{+3} .

The chemical formulas of the vanadium hydrous micas are complex, but the analyses can be approximated by:



Thus the maximum oxygen requirement would be that necessary to change the $(V^{+3},Fe^{+2})_{0.6}$ to $(V^{+4},Fe^{+3})_{0.6}$ or about 0.15 mols O_2 . Therefore, the oxygen demand ranges somewhere between zero and 0.15 mols per mol of vanadium hydromicas. That for the vanadium chlorites is presumably about the same.

Summary of oxygen requirements

The amount of oxygen required for maximum oxidation of the various primary minerals of the Plateau ores is given in table 1.

Table 1.--Summary of maximum oxygen demand for oxidation of some typical plateau minerals.

Mineral	Oxidation products	Mols O_2 /mol mineral
Pyrite	Fe_2O_3 and SO_4^{--}	3 3/4
Chalcopyrite	$Cu_2(OH)_2CO_3$, Fe_2O_3 and SO_4^{--}	4 1/4
Montroseite	Hewettite	1/2
Montroseite + pitchblende	Carnotite	1 (per 1 mol each of reactants)
Pitchblende	Uranyl oxide, sulfate, or carbonate	1/2
Vanadium chlorite	Oxidized vanadium chlorite	} 1/7 (approximately)
Vanadium hydrous mica	Oxidized vanadium mica	
Vanadium mica	Does not oxidize	0

Oxidation of a typical uranium-vanadium ore

Consider the oxidation of an ore containing pitchblende 0.5 percent, montroseite 4 percent, vanadium hydromica 6 percent, and pyrite 6 percent by weight, with the remainder chiefly quartz and other unreactive detrital minerals. Each ton of ore contains 16.8 mols of pitchblende, 433 mols of montroseite, 456 mols of pyrite, and 146 mols of vanadium silicate.^{1/}

The final result of natural oxidation might convert the iron of pyrite to ferric oxide, and the sulfide to sulfate; montroseite and pitchblende would oxidize to carnotite and the excess montroseite to hewettite. Assuming original V^{+3} and Fe^{+2} in the structure of the hydrous mica, the vanadium would be changed from trivalent to quadrivalent, and the iron from bivalent to trivalent.

^{1/} This figure must be considered a rough approximation because of the variability of the vanadium and iron content of the silicates.

The oxygen requirements can be determined from table 1.

	Mols O ₂ required
17 mols pitchblende + 17 mols montroseite	17
416 (433-17) mols montroseite	208
456 mols pyrite	1710
146 mols vanadium hydromica	21
Total mols O ₂ per ton of ore	<hr/> 1956
Total pounds O ₂ per ton of ore	137

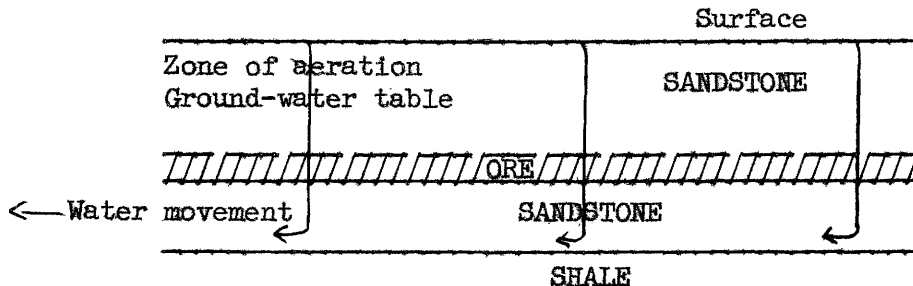
It is of interest to assess the two chief mechanisms by which oxidation can occur in terms of this oxygen requirement. Oxidation can be accomplished either by air moving in and out of damp rock or by oxygenated ground waters flowing through the ore. In the former case, oxidation would take place in a thin film of adsorbed water on the rock grains. In the latter, oxidation would take place below the water table, in the former above it.

Air is 21 percent by weight oxygen; thus it would require about $\frac{137}{0.21} = 650$ pounds of air for complete oxidation by a "breathing" or "moist air" process. At earth-surface condition, 650 pounds of air occupy about 250,000 liters, or about 8,800 cubic feet. A ton of ore occupies about 15 cubic feet; with 10 percent porosity it could accommodate about 1.5 cubic feet of air. Thus, for final oxidation the air in a given volume of ore would have to be changed $\frac{8800}{1.5} = 5850$ or about 6,000 times.

On the other hand, if oxidation occurs below the water table through the agency of air-saturated water, about 8,000,000 liters of water would be required per ton of ore, for the solubility of air in water is only about 20 milliliters per liter, and its oxygen content is about 6 milliliters per liter.

In other words, about 280,000 cubic feet of water would have to pass through each ton of ore. Assuming 10 percent porosity and ideal permeability, this would mean refilling of the volume occupied by one ton 185,000 times.

From these considerations it appears that "moist air" oxidation above the water table could be far more rapid than oxidation by air-saturated water below it. For example, if an ore layer three feet thick, of the composition assumed, occurred just below the water table, so that oxidation had to take place by air dissolved in the ground water draining downward through the ore, 56,000 cubic feet of water would have to drain through each square foot of surface to oxidize the ore completely (as illustrated below). The source of water, under the condition shown, would be rain.



Inasmuch as the amount of water now being added to the zone of saturation by rain is probably negligible because of loss by evaporation and transpiration, oxidation by such a mechanism is undoubtedly much slower than by circulating air.

Large volumes of water and long time intervals are involved if it is assumed that oxidation is by aerated water moving laterally through an ore-bearing layer. Under these circumstances the ore would have to be oxidized sequentially in the direction of water movement. Each linear foot of ore oxidized would require about 185,000 linear feet of water flow. At common

rates of ground-water movement of a few feet per year in moderately permeable media, several million years would be required to oxidize an ore body a hundred feet long, even if the entering water were fully aerated.

Inasmuch as the reducing capacity of rocks is such that the oxygen content of ground water disappears at or near the water table, and as a result conditions below the water table are reducing, oxidation of ores beneath the water table must be extremely slow or lacking under all but unusual conditions of very rapid circulation.

In summary, oxidation of the Colorado Plateau uranium ores probably has taken place after the water table dropped below the ore zones.

Important, perhaps, is the demonstration of the difficulty of moving deposits by lateral migration of ground water during the geologic past, when the rocks were saturated with water. If uranium and vanadium were moved, it appears unlikely that the process involved was an oxidation-transportation-reduction and deposition cycle, where laterally moving phreatic waters act as both oxidizing and transporting agents. The oxygen (or equivalent) demand for large-scale oxidation in water-saturated rocks is large, and ground waters are characteristically anaerobic.

The conclusion drawn is not new; long ago Spencer (1917) deduced that oxidation of copper ores under semiarid conditions takes place above the water table in a film of moisture on the mineral grains. Describing the copper deposits at Ely, Nevada, he says (p. 80-81): "By considering the amount of oxygen that water can absorb by contact with the air under atmospheric pressure at 7,000 feet elevation and at the present mean annual temperature of the region, it is found that, even if precipitation in the past has been 25 percent greater than at present, and that as much as 60 percent of the rainfall could have penetrated to the ore body, the oxygen

required to oxidize 500 feet of ore like that now existing would require the contributions of rainfall during a period longer than physicists and geologists are willing to allow for the age of the earth. [Spencer assumed 60,000,000 years at that time.] Although all the assumptions made tend to a minimum, the time required, as calculated in this way, is still so immoderately great as to demand a different hypothesis in regard to the manner in which oxygen has been delivered to the place of sulfide decomposition. It is thought, therefore, that a large part of the oxygen must have been derived from air that circulated through the oxidizing capping... It would seem, then, that the greater part of the oxidation must take place when the sulfides are moist rather than when they are flooded..."

THE REDUCING EFFECT OF WOODY MATERIALS 2/

It is well known that many reduced uranium ores are associated with woody material; impregnation and replacement of woody material by pitchblende, coffinite, montroseite, and pyrite in ore-bearing material are quite common. Is it possible that such ores were deposited by the reducing action of woody material upon oxidized mineralizing solutions carrying vanadium (V) and uranium (VI) ions?

Because interest here is in a quantitative appraisal of the reduction requirement, it becomes necessary to determine the reducing capacity of woody material, so that the amount of woody material necessary to produce a typical ore can be calculated. To do this it is first necessary to consider some aspects of the chemistry of woody material; as no experimental values of reducing capacity of woody material in solutions containing

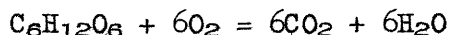
2/ Extracted from a dissertation presented by Alfred M. Pommer to Georgetown University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

uranium (VI) and/or vanadium (V) have been found in the literature, it was necessary to determine this factor experimentally, using conditions approaching the geological environment within the limits of the laboratory.

Some aspects of wood chemistry

Wood usually contains moisture ranging up to 10 percent and a fraction of a percent ash (Lange, 1949). The dry matter contains 40-50 percent cellulose, 10-30 percent hemicellulose, and 20-30 percent lignin. Cellulose and hemicellulose are polymers of glucose or its isomers. Some sugars of slightly different composition, such as xylose, are present, but they do not change the calculated results significantly and may be treated as glucose.

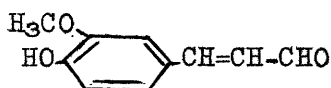
In the presence of a strong oxidizing agent glucose is decomposed according to the following reaction:



One mol (180 g) of glucose then requires 24 equivalents to oxidize it completely; it has an equivalent weight of 7.5.

The cellulose monomer is $\text{C}_6\text{H}_{10}\text{O}_5$ with a molecular weight of 162. For complete oxidation: $\text{C}_6\text{H}_{10}\text{O}_5 + 6\text{O}_2 \longrightarrow 6\text{CO}_2 + 5\text{H}_2\text{O}$. Thus cellulose or its monomer, assuming complete oxidation to CO_2 and H_2O , also requires 24 equivalents and its equivalent weight is 6.75. In other words 100 grams of cellulose has a theoretical reducing capacity of 14.8 equivalents, or 14,800 milliequivalents.

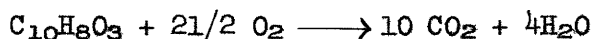
The oxidation of lignin is much more complicated. Klason (1920) postulated lignin to be a polymer of coniferyl alcohol or coniferyl aldehyde



and this belief is currently accepted by many (Gortner, 1949). Assuming complete oxidation of the coniferyl aldehyde monomer to CO_2 and H_2O gives an equivalent weight of 4.05 and a reducing capacity of 24,700 milliequivalents per 100 g, almost twice that of cellulose, according to the reaction:



If a formula for lignin proposed by Russell (1948) is used, the summary equation is:



The equivalent weight is 4.03 and the reducing capacity of 24,900 meq/100 g. These two examples illustrate that different proposed lignin structures do not differ greatly in reducing capacity.

We have no assurance, of course, that cellulose or lignin are completely oxidized.

Experimental determination of reducing capacities of some material

A series of experiments was carried out to determine the reducing capacity of wood. When wood is placed in an acidified solution of ammonium vanadate at room temperature and pressure, a green color is observed after a few days, indicating partial reduction of V(V) to V(IV) .^{3/} However, to simulate conditions in nature, experiments were run at 150°C , a temperature representing a consensus of several of our coworkers of the temperature of formation of the ores. Determinations of reducing capacity were carried out according to the following procedure: a 10 mg sample was placed together with 10 ml 0.1 N $(\text{VO}_2)_2\text{SO}_4$ solution containing an excess of free sulfuric acid and some Na_2SO_4 in a Pyrex tube, sealed,

^{3/} It also was possible to reduce V(IV) solutions to V(III) with wood at elevated temperatures.

and heated at 150° C at an estimated pressure of 70 psi (ignoring the boiling point elevation of the solution by the added electrolytes) for three days; at the end of the run the reduced vanadium was titrated potentiometrically. Any remaining sample was recovered, washed, dried, and weighed. Results are shown in table 2. From the data two sets of reducing-capacity values were obtained. The first set is the milliequivalents of vanadium reduced per 100 grams of original sample, the second set is the milliequivalents of vanadium reduced per 100 grams of wood or lignite decomposed (wood decomposed = original sample minus solid residue).

As the experimental results were 58 percent of the calculated results, an attempt was made to obtain reducing capacities closer to the calculated value by extending the time of the run to twelve days. This attempt was not successful. Although it was possible to increase the reducing capacity of glucose under parallel conditions from 8900 meq/100 g to an apparent 10,000 meq/100 g by increasing the heating time from 3 to 12 days, the reducing capacities of wood and lignite samples were of the same order of magnitude in the 3 day runs and in the 12 to 13 day runs, with some of the long runs giving slightly lower reducing capacities. There are two possible explanations for this phenomenon, both probably contributing simultaneously: it was noted in the blank runs that the vanadate solution on heating gave a brown precipitate, which gave an X-ray pattern of $V_2O_5 \cdot H_2O$. If we consider that we have two competing reactions, one the precipitation of the vanadium(V) oxide which removes it from the reaction, and the other the reduction of the VO_2^+ ion by the slowly decomposing polymers of the woody material, it can be seen that relatively soon a point is reached where the concentration of vanadium(V) ions in the solution is so low that reduction becomes very slow and in effect ceases. The other

Table 2.--Reducing capacity of wood and lignite.

	Wood (a) <u>meq/100 g</u>	Lignite (b) <u>meq/100 g</u>
Calculated reducing capacity (c)	15800	14600
Experimental reducing capacity (d)	10300 5100 9700	5600 6800 8200
Average experimental reducing capacity	8400	6900
Experimental reducing capacity corrected for insoluble constituents (e)	11300 7100	8600 8400
Average corrected reducing capacity (f)	9200	8500
Average corrected reducing capacity expressed as percentage of calculated reducing capacity	58%	58%

- (a) Fresh spruce (*Picea excelsa* Lk) containing 58 percent cellulose and 29 percent lignin (Varossieau and Breger, 1951).
- (b) Lignite from the Beulah-Zap bed, Dakota Star mine, Mercer County, N. Dak., containing 41.2 percent moisture and ash (Analyst, R. T. Moore, U. S. Geological Survey).
- (c) For details of calculation see text.
- (d) All reducing capacities were determined by potentiometric titration of the product obtained by heating a 10-mg sample with 10 ml of a 0.1-formal vanadium (V) solution acidified to a pH of 0.7 in a sealed Pyrex tube for 3 days at 150° C. All values were corrected for a blank (0.15 ml).
- (e) The undecomposed residue was isolated, washed, dried, and weighed, and the reducing capacity of the decomposed portion calculated. This was done on duplicate samples only owing to experimental difficulties on the triplicate run.
- (f) This value was rounded off to 9000 in both samples for use in table 3.

reaction is the formation of high-carbon polycyclic compounds by partial degradation of the wood which loses hydrogen and oxygen atoms during oxidation and results in reaction products becoming increasingly more resistant to attack. In the case of glucose this phenomenon does not take place.

The calculated reducing capacities used in table 2 were obtained as follows: The theoretical reducing capacity of a fresh spruce of the given composition is computed, assuming complete oxidation to CO_2 and H_2O and using the Russell formula for lignin. A 100-gram sample contains 58 g cellulose with a reducing capacity of $(0.58 \times 14,800)$ 8600 milliequivalent per 100 g; it also contains 29 g lignin with a reducing capacity of $(0.29 \times 24,800)$ 6700 milliequivalent per 100 grams, giving a total reducing capacity of 15,300 milliequivalent per 100 grams. The experimental value at pH 0.7 corrected for undecomposed matter is 9200 milliequivalents per 100 grams, or 58 percent of the theoretical maximum value.

The reducing capacity of the lignite used is substantially that of wood; this was an unexpected result. The chemistry of lignite is little known, but Breger (1951) has presented evidence based on infrared spectra that the skeletal structures of humic acid and lignin are related and suggested that they may even be identical. Let us now assume that the reducing capacities of lignin and humic acid are the same. Let us next assume that lignite consists of moisture, ash, and humic acid only; we know that this is not quite correct, but this assumption would leave us with the same carbon content for lignite as for lignin. The carbon content of Russell lignin is 66 percent and its carbon-hydrogen ratio is 100:7.4; both of these values are not markedly different from typical lignite values and our assumption may not be far off. Because our lignite has a moisture and ash content of 41.2 percent, it now is assumed to contain 58.8 percent humic

acid (reducing capacity 24,800 meq/100 g) and its reducing capacity assuming total oxidation is $(0.588 \times 24,800)$ 14,600 meq/100 g. The experimental value of 8500 meq/100 g then indicates either incomplete oxidation or the transition of some of the humic acid to fixed carbon, which is not too unlikely in a lignite. To investigate whether the oxidation of cellulose, lignin, wood, and lignite by vanadium(V) solutions proceeds to CO_2 and H_2O at least in part or whether it does not proceed at all beyond some intermediate state, the reaction products of these substances with vanadium(V) solutions were examined by infrared spectroscopy; carbon dioxide was identified in all samples (R. G. Milkey, analyst, personal communication).

Amount of reducing agent required

If primary ore was deposited by the reduction of solutions carrying quinquevalent vanadium and sexivalent uranium ions, it may now be possible to make rough estimates of the concentration of wood or lignite necessary for precipitation of a typical ore. Unfortunately, the requirement in terms of equivalents of reducing agent is not necessarily the same as equivalents of oxygen necessary to oxidize low-valent ore minerals as shown in table 1.

For oxidation the primary mineral assemblage is reasonably well known as are the oxidation products. It is not necessary to distinguish between minerals already present in the rock before ore deposition and those superimposed during mineralization. Any pyrite present in an ore body becomes oxidized eventually, whether it is syngenetic, diagenetic, or epigenetic.

Therefore, it may be instructive to calculate the weight percent of fresh spruce or lignite necessary to precipitate each ore mineral from aqueous solution by reduction from a specified ion.

In this connection it must be noted that it is impossible to make an intelligent allowance for pyrite. In the first place, it is impossible to make a valid correction for syngenetic or diagenetic pyrite, which must be deducted from the total pyrite in the ore. Also no accurate correction can be made for other sulfides or sulfur compounds in the organic matter available for the reduction of possible ferric iron carried in a mineralizing solution. Finally, in the absence of sulfide made available by the woody material and free hydrogen sulfide fortuitously present in the system (which of course also would reduce vanadium and uranium ions) any pyrite sulfur must be produced by reduction of sulfate ions. Under 200° C, reduction of sulfate ions to sulfide or polysulfide in nature is known only in the presence of certain micro-organisms (e.g. Sporovibrio).

Table 3 is a compilation of data which, it is hoped, will enable its user to compute the amount of woody material required to precipitate an ore containing a given amount of montroseite, pitchblende, and vanadium clay. He can then judge whether the amount of carbonaceous material expected in the formation under consideration is sufficient to make this process probable. It can be seen from the calculations that woody material can easily be present in sufficient amounts to deposit typical ore concentrations from oxidized solutions by reduction, but, of course, this does not hold in every case. Subbituminous and higher rank coals may be expected to behave like lignite.

Some typical reduction equations

Finally, it may be of interest to demonstrate some possible reducing reactions by writing down some speculative equations showing the reduction of uranyl and vanadate ions by cellulose (represented by $C_6H_{10}O_5$, its

Table 3.--Amount of reducing material required for the deposition of some reduced minerals from oxidized solutions.

Mineral species formed	Formula	Oxidized species in solution	Concentration of mineral species in sediment	Fresh spruce or lignite required			
				Wt% Lb/ton	%C	Wt% Lb/ton	%C
Pitchblende	UO ₂	UO ₂ ⁺⁺	1 Wt% of mineral	0.048	0.96	0.082	1.6
			1 Lb/ton of mineral	0.002	0.048	0.004	0.082
			1 Wt% of U	0.055	1.10	0.092	1.8
			1 Lb/ton of U	0.002	0.055	0.005	0.092
Montroseite	VOOH	VO ₂ ⁺	1 Wt% of mineral	0.15	3.1	0.26	5.3
			1 Lb/ton of mineral	0.008	0.15	0.013	0.26
			1 Wt% of V	0.25	5.1	0.44	8.8
			1 Lb/ton of V	0.013	0.25	0.022	0.44
V-silicates V-mica V-hydromica V-chlorite	(Mol. wt. 373)	VO ₂ ⁺	1 Wt% of mineral	0.034	0.68	0.060	1.2
			1 Lb/ton of mineral	0.002	0.034	0.003	0.060
			1 Wt% of V	0.25	5.1	0.44	8.8
			1 Lb/ton of V	0.013	0.25	0.022	0.44

Notes

Values used in construction of table: "Theoretical" equivalent weight of wood or lignite: 6.5; this weight was obtained by averaging the equivalent weight for wood (6.3) and lignite (6.8) obtained from the calculated reducing capacities given in the text by the conversion formula; equivalent weight (in g) = 100000:reducing capacity (in meq/100 g). The "experimental" value was obtained from the rounded-off reducing capacity of 9000 meq/100 g.

Both the wood and the lignite contained about 45 percent C (actual values: wood 46 percent, lignite 42 percent). 1% V₂O₅ = 0.56% V; 1% U₃O₈ = 0.85% U

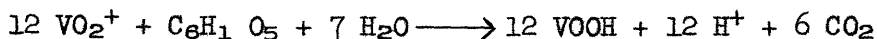
Sample calculation: 1) An ore contains 50 lb/ton montroseite, and 100 lb/ton pitchblende. What is the theoretical amount of lignite required for deposition?

Answer: 50 x 0.15 + 100 x 0.048 = 12.3 lb/ton or about 0.6 wt % lignite.

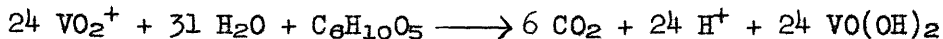
- 2) Ore content: 2% V₂O₅ and 0.5% U₃O₈
Lignite required: 2 x 0.56 x 0.25 + 0.5 x 0.85 x 0.055 = 0.5 wt %

monomer). Of course, it is also possible to write similar reactions for lignin.

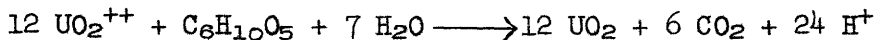
Reduction of vanadium(V) ion to montroseite



Reduction of vanadium(V) ion to duttonite



Reduction of uranyl ion to pitchblende



SUMMARY AND GEOLOGIC APPLICATION

It has been assumed that uranium and vanadium ores of the Colorado Plateau originally were in a reduced form and have been oxidized subsequently. This oxidation was carried on by moist air above the water table. The reduced ore may have been deposited either from reduced or oxidized solutions. In the latter case woody materials are a likely precipitating agent, and it is possible to appraise their sufficiency in a given environment from reducing capacities.

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